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Studies on 1,3-Dithiolium Cations. II[1]. Reactions of 4-Phenyl Derivatives with Nucleophilic Reagents

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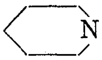
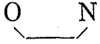
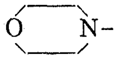
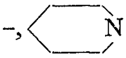
Nucleophilic reagents attacked exclusively to C–2 position of 4-phenyl-1,3-dithiolium cation derivatives and the corresponding 1,3-dithioles were obtained in good yields. Thus, 2-amino-, 2-aminothiocarbonylthio-, 2-phenylthio-1,3-dithioles were yielded. $LiAlH_4$ reduction furnished 1,3-dithiole and hydride abstraction gave original cation. 1,3-Dithiolium cation acted as a Brönsted acid and conjugate base carbinol was isolated. Similarly, covalent 2-alkoxy compounds were easily obtained and regenerated cation by the action of acid. Grignard reaction toward cation opened the new routes to 2-substituted 1,3-dithiolium cations.

In the previous paper,[1] a convenient method for the synthesis of 1,3-dithiolium salt derivatives was reported. We wish to report some reactions of 4-phenyl-1,3-dithiolium derivatives with nucleophilic reagents, giving the corresponding dithiole derivatives.

When 4-phenyl-1,3-dithiolium hydrogen sulfate (I: R=R′=H, X=HSO_4) was refluxed with secondary amines in acetone to give 2-amino-1,3-dithiole derivatives in good yields which were found to be identical with the amines (II: $^{R}_{R'}\!>\!N$ = -, -, $^{CH_3}_{C_6H_5CH_2}\!>\!N-$) obtained from 2-immonium salts by $NaBH_4$ reduction.[1] Similarly, the reaction with dithiocarbamoyl salts gave the corresponding 2-dithiocarbamate (III: $^{R}_{R'}\!>\!N$ = -, -, $^{CH_3}_{CH_3}\!>\!N-$) The products obtained exhibited C–2 and C–5 protons in NMR spectra, showing the introduction of dithiocarbamate groups to C–2 position. Reaction with sodium phenylmercaptide gave 2-phenylmercapto compound IV. Reduction with $LiAlH_4$ gave 4-phenyl-1,3-dithiole (V)[4] in good yield. NMR spectrum exhibited C–5 proton at 3.72 τ and C–2 methylene protons at 5.50 τ as singlets. V was treated with triphenylmethyl perchlorate to abstract hydride anion giving 1,3-dithiolium perchlorate easily. V is iso-π-electronic with tropylidene (cycloheptatriene) and V was oxidized with SeO_2 to give phenyl isodithione (VI)[3,4] iso-π-electronic with tropone (VII). Isodithione VI was expected to have the unsaturation character due to ketonic structure and aromatic character due to polar 6π-structure from the resonance contributions. IR spectrum of VI exhibited C=O band at 1641 cm^{-1} shifting to longer wave length than normal carbonyl band (1775 cm^{-1} in S,S′-ethylenedithiocarbonate).[5] This value is close to that of carbonyl band in tropone (VII) (1581—1613 cm^{-1}).[6] NMR spectrum exhibited C–5 proton's signal at lower field, 3.20 τ in $CDCl_3$, than other dithioles. These facts suggest that VI was effected by partial polar structual contribution (VI′).[3]

Treatment of perchlorate I with triethylamine gave dimer VIII[3,7] immediately. Recently, Olofson, *et al.*[8] reported the formation of tetrathiomethoxyethylene from dithiomethoxy-

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[1] Part I: A. Takamizawa and K. Hirai, *Chem. Pharm. Bull.* (Tokyo), 17, 1924 (1969).

[2] Location: *Fukushima-ku, Osaka.*

[3] H. Prinzbach and E. Futterer, "Advances in Heterocyclic Chemistry," Vol. 7, ed. by A. R. Katritzky and A.J. Boulton, Academic Press, New York and London, 1966, pp. 39—151.

[4] H. Behringer and D. Deichmann, *Tetrahedron Letters*, **1967**, 1013.

[5] R. Mayer and B. Gebhardt, *Chem. Ber.*, 97, 1298 (1964).

[6] T. Nozoe, K. Takase, and H. Matsumura, "Daiyuki-kagaku," Vol. 13, Asakura Shoten, Tokyo, 1960, p. 76.

[7] H. Prinzbach, H. Berger, and A. Lüttringhaus, *Angew. Chem. int. Ed.*, 4, 435 (1965).

[8] R.A. Olofson, S.W. Walinsky, J.P. Marino, and J.L. Jernow, *J. Am. Chem. Soc.*, 90, 6554 (1968).

methyl fluoroborate by base treatment *via* dithiomethoxycarbene. The formation of dimer VIII would be explained as the result of a base-induced deprotonation of I, affording 4-phenyl-1,3-dithiolecarbene (XIV) which yielded alkene VIII by the reaction with additional carbonium ion I followed by deprotonation.

Addition of water to 1,3-dithiolium salt I gave a milky suspension, and shaking with ether of this suspension gave a ether solution which afforded the crystals of mp 92° after evaporation and recrystallization from dil. EtOH. Elemental analysis of this product was agreed with the value for hydroxide adduct of the cation. Action of acid gave original cation immediately. Now, it was found that 1,3-dithiolium I was acted as a Brönsted acid and the conjugate base carbinol IX was isolated. It indicates that 1,3-dithiolium salt I is not so stable as keep ionic structure in water. IX was very unstable to decompose to give an oil on standing at room temperature. This decomposition seems to proceed *via* ring opened thiole (X or X').

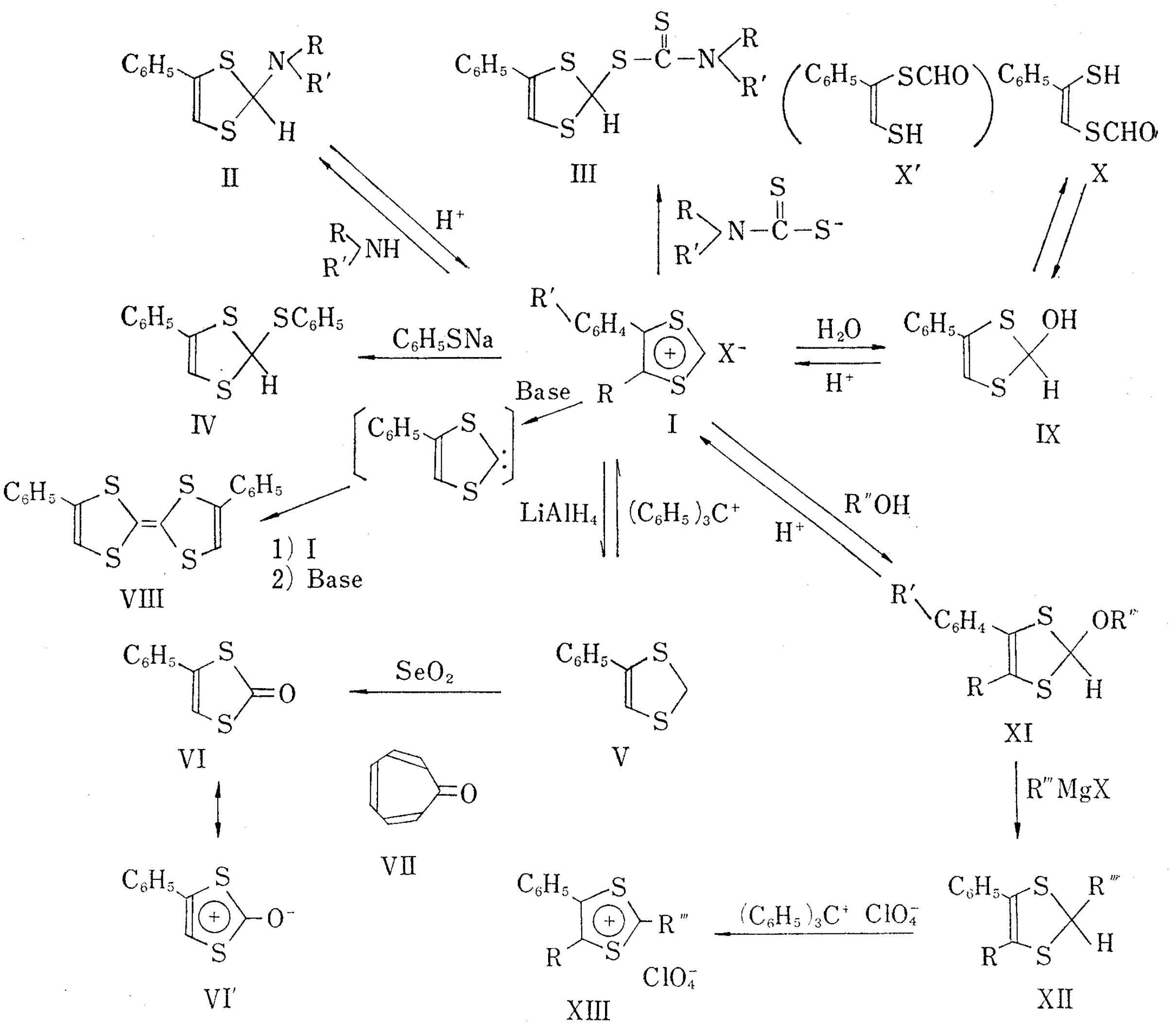

Chart 1

When I was treated with methanol in the presence of dil. $NaHCO_3$ as cyclopropenyl cation was treated,9) covalent 2-methyl ether XI ($R''=CH_3$) was easily obtained. UV spectrum of XI ($R=R'=H$, $R''=CH_3$) was identical with that of I in EtOH previously reported by

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9) R. Breslow, and C. Yuan, *J. Am. Chem. Soc.*, **80**, 5991 (1958); R. Breslow, H. Honer, and H.W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962).

10) D. Leaver, W.A. Robertson, and D.M. McKinnon, *J. Chem. Soc.*, 5104 (1962).

Leaver, *et al.*[10] (Fig. 1.) Therefore, 4-phenyl-1,3-dithiolium salt and related compounds showed UV spectra of covalent 2-ethylethers in Leaver's condition (in EtOH solution containing a little perchloric acid).[11] Similar reaction converted the cations to 2-methoxy-4-*p*-substituted phenyl-1,3-dithioles (XI: R=H, $R''=CH_3$, $R'=CH_3O$, CH_3, Br, Cl, NO_2; $R=C_6H_5$, R′=H, $R''=CH_3$). These covalent methyl ethers were rather stable compared with carbinol IX, and instantly regenerate salts by addition of acids (*e.g.* addition of 70% perchloric acid to an ethereal solution of XI yielded 1,3-dithiolium perchlorate (I) in quantitative yield). Therefore, purification of salts I through 2-methylethers XI is very effective, and XI can be used instead of salts.

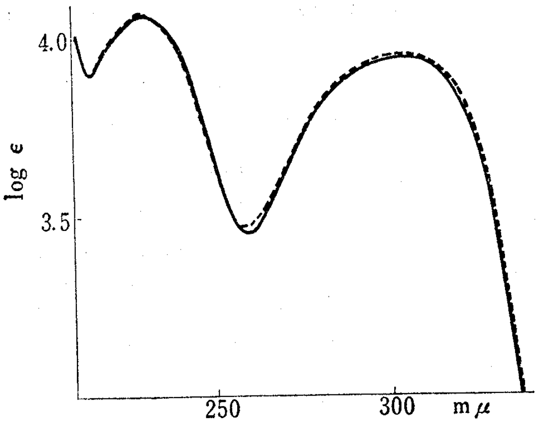

Fig. 1. UV Spectra of 4-Phenyl-1,3-dithiolium Perchlorate (I) (———) and 2-Methoxy-4-phenyl-1,3-dithiole (XI) (------) in EtOH

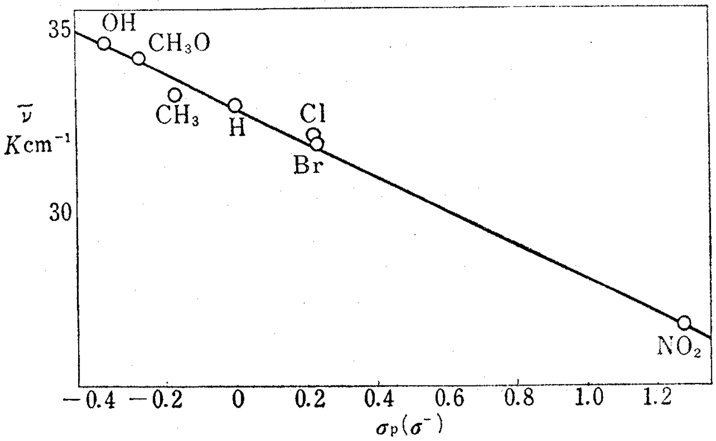

Fig. 2. Correlation of Hammett's σ_p Constant. (σ^- for NO_2) with $\tilde{\nu}$ (K cm^{-1}) of the Longest Wave Length Band of XI

As shown in Fig. 2, there is a linear relationship between σ_p constant (σ^- for NO_2)[12] and wave number of the longest wave length for UV spectra of 2-alkoxy-4-*p*-substituted phenyl-1,3-dithioles (XI).

It is noted that 4-phenyl-1,3-dithiolium salt and related compounds possess a potential utility as a protecting group of alcohol, thiole, or amine, because C–2 position has a high activity towards nucleophilic reagents and regenerates the original components under a mild condition.

The reaction of XI (R=R′=H, $R''=CH_3$) with phenyl magnesium bromide gave 2,4-diphenyl-1,3-dithiole (XII: R=H, $R'''=C_6H_5$) as impure material and was converted directly to 2,4-diphenyl-1,3-dithiolium perchlorate (XIII: R=H, $R'''=C_6H_5$)[10] with triphenylmethyl perchlorate. Similarly, the reaction with *n*-propyl magnesium bromide followed by hydride abstraction gave 2-*n*-propyl-4-phenyl-1,3-dithiolium perchlorate (XIII: R=H, $R'''=n\text{-}C_3H_7$) [mp 95—98°; UV $\lambda_{max}^{50\%\ H_2SO_4}$ 240, 271 (sh), 340 mμ (log ε: 4.21, 3.96, 3.71); NMR (τ) 8.87^t (CH_3–), 6.37^t $\left(CH_2\text{-}\langle^{S}_{S}\oplus\right)$ (J=7 cps), 1.30^s (C–5–H) (in CD_3CN)]. 2,4,5-Triphenyl-1,3-dithiolium perchlorate (XIII: $R=R''=C_6H_5$)[10] was similarly obtained from 2-methoxy-4,5-diphenyl-1,3-dithiole (XI: $R=C_6H_5$, R′=H, $R'''=CH_3$) by Grignard reaction with phenyl magnesium bromide followed by hydride abstraction. The combination of these reactions is a convenient method for the preparation of 1,3-dithiolium salts bearing various substituents at different positions.

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[11] The sensitivity of the shape of the absorption curve of 5-methyl-1,3-benzodithiolium to change in the media has been pointed out by R. Zahradnik ("Advances in Heterocyclic Chemistry," Vol. 5, ed. by A.R. Katritzky, A.J. Boulton and J.M. Lagowski, Academic Press, New York and London, 1965, pp. 1—67). We have reported spectral data of 1,3-dithiolium cation derivatives in Ref. 2).

[12] L.N. Ferguson, "The Modern Structural Theroy of Organic Chemistry," Prentice-Hall, Inc., Englewoods Cliffs, N.J., 1964, p. 415.

Experimental

All melting points were determined in capillary tube and are uncorrected. NMR spectra were taken on a Varian A-60 spectrometer in $CDCl_3$ or CF_3COOD containing TMS as an internal reference and chemical shifts are expressed in a τ value. UV spectra were taken on a Hitachi EPS-3 spectrophotometer in 95% EtOH.

General Procedure for the Preparation of 2-Amino-1,3-dithioles (II)——To a suspension of 0.1 g of 4-phenyl-1,3-dithiolium hydrogen sulfate (I: $R=R'=H$, $X=HSO_4$) in 5 ml of acetone, N,N-methylbenzyl amine was added and refluxed for 10 min. Reaction mixture was concentrated *in vacuo*, H_2O was added to the residue, and extracted with ether. Ether extract was washed with H_2O, dried over anhyd. $MgSO_4$, and evaporated to give oil which crystallized slowly. Yield, 0.1 g (93%). IR spectrum was identical with 2-N,N-methylbenzylamino-4-phenyl-1,3-dithiole $\left(\mathrm{II}:\ \genfrac{}{}{0pt}{}{R}{R'}{>}N-=\genfrac{}{}{0pt}{}{CH_3}{C_6H_5CH_2}{>}N-\right)$ prepared by $NaBH_4$ reduction from immonium compound.[2]

Similarly, morpholine and piperidine were allowed to react with I to give the corresponding 2-morpholino and 2-piperidino-4-phenyl-1,3-dithiole $\left(\mathrm{II}:\ \genfrac{}{}{0pt}{}{R}{R'}{>}N-=\overline{\underline{\mathrm{O}\quad\mathrm{N}}}-\text{ and }\langle\overline{\underline{\quad\ \mathrm{N}}}-\right)$ in 83 and 73% yields, respectively. Identities with authentic samples[2] were confirmed by UV and IR spectral comparisons.

2-Morpholinothiocarbonylthio-4-phenyl-1,3-dithiole $\left(\mathbf{III}:\ \genfrac{}{}{0pt}{}{R}{R'}{>}N-=\overline{\underline{\mathrm{O}\quad\mathrm{N}}}-\right)$——To a suspension of 0.1 g of 4-phenyl-1,3-dithiolium hydrogen sulfate (I: $X=HSO_4$) in 10 ml of acetone, 0.15 g of morpholine morpholinocarbodithioate was added and refluxed for 20 min. Reaction mixture was concentrated *in vacuo*, H_2O was added to the residue, and extracted with ether. Ether extract was dried over anhyd. $MgSO_4$ and evaporated to give 0.13 g (96%) of colorless prisms, mp 119—120°. *Anal.* Calcd. for $C_{14}H_{15}ONS_4$: C, 49.27; H, 4.43; 4.10; S, 37.59. Found: C, 49.79; H, 4.47; N, 4.18; S, 36.45. UV λ_{max}^{EtOH} 233.5, 316 mμ (log ε 4.15, 3.94). NMR: C-2, 5-H 3.07, 3.57 τ ($CDCl_3$).

2-Piperidinothiocarbonylthio-4-phenyl-1,3-dithiole $\left(\mathbf{III}:\ \genfrac{}{}{0pt}{}{R}{R'}{>}N-=\langle\overline{\underline{\quad\ \mathrm{N}}}-\right)$——I and piperidine piperidinocarbodithioate were treated as above to give colorless prisms, mp 119—120°, in 74% yield. *Anal.* Calcd. for $C_{15}H_{17}NS_4$: C, 53.10; H, 5.05; N, 4.13; S, 37.73. Found: C, 53.28; H, 4.98; N, 4.09; S, 37.83. UV λ_{max}^{EtOH} 234, 317 mμ (log ε 4.12, 3.90). NMR: C-2, 5-H 3.05, 3.57 τ ($CDCl_3$).

2-Dimethylaminothiocarbonylthio-4-phenyl-1,3-dithiole (III: $R=R'=CH_3$)——I and sodium N,N-dimethylaminocarbodithioate were treated as above to give colorless prisms, mp 78—79°, in 45% yield. *Anal.* Calcd. for $C_{12}H_{13}NS_4$: C, 48.16; H, 4.38; N, 4.68; S, 42.78. Found: C, 47.95; H, 4.26; N, 4.83; S, 42.54. UV λ_{max}^{EtOH} 234, 315 mμ (log ε 4.12, 3.91). NMR: C-2, 5-H 3.15, 3.57 τ ($CDCl_3$).

2-Phenylthio-4-phenyl-1,3-dithiole (IV)——To a solution of 0.022 g of metalic Na in 8 ml of abs. EtOH, 0.10 g of thiophenol was added to give sodium thiophenolate. To this solution, 0.2 g of 4-phenyl-1,3-dithiolium hydrogen sulfate (I: $X=HSO_4$) was added and refluxed for 1 hr. Reaction mixture was concentrated *in vacuo*, and petroleum benzine was added to the residue to give 0.134 g (66%) of colorless needles, mp 81—82°. *Anal.* Calcd. for $C_{15}H_{12}S_3$: C, 62.50; H, 4.20; S, 33.30. Found: C, 62.61; H, 4.25; S, 33.22. UV λ_{max}^{EtOH} 221, 320 mμ (log ε 4.25, 3.85). NMR: C-2, 5-H 3.80, 3.84 τ ($CDCl_3$).

4-Phenyl-1,3-dithiole (V)——To a suspension of 0.2 g of 4-phenyl-1,3-dithiolium hydrogen sulfate (I: $X=HSO_4$) in 15 ml of abs. ether, 0.05 g of $LiAlH_4$ was added and stirred for 1 hr at room temperature. Aqueous NaOH solution was added to the reaction mixture to decompose and decanted ether layer. Ether layer was dried over anhyd. $MgSO_4$ and evaporated to give 0.12 g (92%) of pale brown prisms, mp 45—48°. *Anal.* Calcd. for $C_9H_8S_2$: C, 60.00; H, 4.48; S, 35.53. Found: C, 59.62; H, 4.40, S, 35.34. UV λ_{max}^{EtOH} 245, 342 mμ. NMR: C-2, 5-H 5.50 (2H), 3.72 τ.

Hydride Abstraction of V——Triphenylcarbinol (0.1 g) was dissolved in 1 ml of Ac_2O by warming on a steam bath. To the solution, 70% $HClO_4$ was dropwise added under cooling to separate trityl perchlorate,[13] which was collected and washed with AcOEt. To a solution of 0.07 g 4-phenyl-1,3-dithiole (V) in 1 ml of AcOH, trityl perchlorate was added and warmed on the steam bath for 2 min. After cooling, ether was added to the reaction mixture, separated crystals were collected, and washed with AcOEt to give 4-phenyl-1,3-dithiolium perchlorate.

4-Phenyl-1,3-dithiol-2-one (VI)——To a solution of 0.2 g of 4-phenyl-1,3-dithiole (V) in 10 ml of dioxane, 0.12 g of SeO_2 was added and refluxed for 1 hr. Reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was subjected to the alumina column chromatography to give pale yellow needles, mp 84—89°. *Anal.* Calcd. for $C_9H_6OS_2$: C, 55.68; H, 3.12; S, 33.01. Found: C, 55.31; H, 3.19; S, 33.09. UV λ_{max}^{EtOH} 220, 285 mμ. IR $\nu_{C=O}$ 1641 cm^{-1} ($CHCl_3$). NMR: C-5H 3.20 τ ($CDCl_3$).

2-Hydroxy-4-phenyl-1,3-dithiole (IX)——To a suspension of 0.2 g of 4-phenyl-1,3-dithiolium hydrogen sulfate (I: $X=HSO_4$) in ether, H_2O was added and shaked. Ether layer was separated, dried over anhyd.

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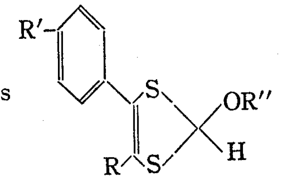
13) H.J. Dauben, Jr., L.R. Honner, and K.M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

$MgSO_4$, and evaporated to give pale brown prisms, mp 90—92°. *Anal.* Calcd. for $C_9H_8OS_2$: C, 55.10; H, 4.11; S, 32.69. Found: C, 55.88; H, 4.06; S, 32.23. UV λ_{max}^{EtOH} 232.5, 308.5 mμ (log ε 4.06, 3.92). IR ν_{OH} 3571 cm^{-1} (CCl_4).

General Procedure for the Preparation of 2-Alkoxy-4-phenyl-1,3-dithioles XI——4-Phenyl-1,3-dithiolium perchlorate (3.0 g) was dissolved in 80 ml of MeOH by warming on a steam bath. To this solution, 30 ml of 10% $NaHCO_3$ solution was added and the solution was evaporated *in vacuo*. H_2O was added to the residue and separated crystals were collected. Recrystallization from dil. EtOH gave 2.2 g (97%) of colorless needles, mp 61° (Table I, II).

TABLE I. 2-Alkoxy-1,3-dithioles



XI

Compd. No.	R	R′	R″	mp (°C)	Yield (%)	Formula	Analysis (%) Calcd. C	H	S	Found C	H	S
1	H	H	OCH_3	61	97	$C_{10}H_{10}OS_2$	57.14	4.80	30.36	57.09	4.69	30.20
2	H	OCH_3	OCH_3	50—52	91	$C_{11}H_{12}O_2S_2$	55.00	5.04	26.70	55.11	4.96	26.57
3	H	CH_3	OCH_3	oil	94							
4	H	Br	OCH_3	43—44	97	$C_{10}H_9OS_2Br$	41.53	3.14	22.17	41.55	3.14	22.26
5	H	Cl	OCH_3	32—34	90	$C_{10}H_9OS_2Cl$	49.06	3.70	26.20	49.15	3.78	26.16
6	H	NO_2	OCH_3	116—117	90	$C_{10}H_9O_3NS_2$	47.06	3.56	25.13	46.92	3.62	25.31
7	C_6H_5	H	OCH_3	67—68	96	$C_{16}H_{14}OS_2$	67.12	4.93	22.40	66.59	4.96	21.78
8	C_6H_5	H	OC_2H_5	78—80	90	$C_{17}H_{16}OS_2$	67.99	5.37	21.36	67.82	5.39	21.03

TABLE II. Spectral Data of 2-Alkoxy-1,3-dithioles XI

Compd. No.	R	R′	R″	UV λ_{max}^{EtOH} mμ (log ε)	NMR[a] C–2,5H, $CH_3O\langle^{S}_{S}$
1	H	H	OCH_3	231, 305 (4.08, 3.94)	3.05, 3.45, 6.72
2	H	OCH_3	OCH_3	237, 290 (3.98, 4.07)	3.13, 3.67, 6.73
3	H	CH_3	OC_2H_5	232, 303 (4.02, 3.91)[c]	
4	H	Br	OCH_3	241.5, 314 (4.12, 4.08)	3.13, 3.53, 6.77
5	H	Cl	OCH_3	236, 312 (4.11, 4.05)	3.07, 3.47, 6.73
6	H	NO_2	OCH_3	258, 373 (4.02, 4.11)	3.07, 3.22, 6.73
7	C_6H_5	H	OCH_3	294, 327 (3.46, 3.46)	3.35, 6.56
8	C_6H_5	H	OC_2H_5	290, 328 (3.80, 3.79)	3.40, [b]
9	H	OH	OC_2H_5	233.5, 289 (3.95, 4.07)[c]	

a) Spectra were taken in $CDCl_3$ containing TMS as an internal reference.
b) Ethyl group as a triplet at 8.75 τ (J=7 cps) and a quartet at 6.28 τ (J=7 cps).
c) Perchlorate (I) was dissolved in 95% EtOH and spectrum was taken.

2,4-Diphenyl-1,3-dithiolium Perchlorate (XIII: R=H, R‴=C_6H_5)——To a suspension of 0.09 g of metalic magnesium in 25 ml of abs. ether, 0.5 g of phenyl bromide and a small amount of I_2 were added and a suspension was stirred with reflux for 2 hr to get phenyl magnesium bromide solution. To this solution, 0.27 g of 2-methoxy-4-phenyl-1,3-dithiole (XI: R=R′=H, R″=CH_3) was added and a solution was stirred with reflux for 1.5 hr. Saturated NH_4Cl solution was added to the reaction mixture to decompose and ether layer was decanted. Ether layer was washed with H_2O, dried over anhyd. $MgSO_4$, and evaporated to give the residual oil. To a solution of this oil in 2 ml of AcOH, trityl perchlorate (prepared from 0.3 g of triphenylcarbinol, 3 ml of Ac_2O, and 0.3 ml of 70% $HClO_4$) was added and a solution was warmed for 2 min on a steam bath. Ether was added to the reaction mixture and separated brown precipitate was collected and washed with AcOEt to give 0.4 g (87%) of pale brown crystals. Recrystallization from AcOH–$HClO_4$ gave pale brown scales, mp 188—189° (decomp.). *Anal.* Calcd. for $C_{15}H_{11}O_4S_2Cl$: C, 50.75; H, 3.15, S, 18.05; Cl, 10.00.

Found: C, 50.66; H, 3.25; S, 18.25; Cl, 9.85. UV $\lambda_{max}^{50\% H_2SO_4}$ 243, 277 (sh), 310, 394 mμ (log ε 4.38, 4.05, 3.95, 4.35). NMR: C-5H 1.22 τ (CF_3COOD).

2,4,5-Triphenyl-1,3-dithiolium Perchlorate (XIII: R=R‴=C_6H_5)——To a Grignard solution prepared from 0.14 g of Mg, 0.9 g of phenyl bromide, and abs. ether, 0.45 g of 2-methoxy-4,5-diphenyl-1,3-dithiole (XI: R′=H, R=C_6H_5, R″=CH_3) was added and a reaction mixture stirred with reflux for 2 hr. Saturated NH_4Cl solution was added and ether layer was decanted. Ether layer was dried over anhyd. $MgSO_4$ and evaporated to give the residual oil. To a solution of this oil in 3 ml of AcOH, trityl perchlorate (prepared from 0.45 g of triphenylcarbinol, 4 ml of Ac_2O, and 0.3 ml of 70% $HClO_4$) was added and a solution was warmed on a steam bath for 2 min. Ether was added to the reaction mixture and separated precipitate was collected and washed with AcOEt. Recrystallization from AcOH–$HClO_4$ gave 0.3 g (46%) of pale yellow prisms, mp 203—205° (decomp.). *Anal.* Calcd. for $C_{21}H_{15}O_4S_2Cl$: C, 58.53; H, 3.57; S, 14.88; Cl, 8.23. Found: C, 58.23; H, 3.57; S, 14.80, Cl, 8.32. UV $\lambda_{max}^{50\% H_2SO_4}$ 231 (sh), 253 (sh), 310, 403 mμ (log ε 4.35, 4.14, 4.00, 4.19).

2-*n*-Propyl-4-phenyl-1,3-dithiolium Perchlorate (XIII: R=H, R‴=*n*-C_3H_7)——To a Grignard solution prepared from 0.1 g of Mg, 0.5 g of *n*-propyl bromide, and abs. ether, 0.4 g of 2-methoxy-4-phenyl-1,3-dithiole (XI: R=R′=H, R″=CH_3) was added and treated as above. Hydride abstraction was carried out by trityl perchlorate to give 0.4 g (66%) of crystals. Recrystallization from AcOH–$HClO_4$ gave colorless scales, mp 95—98°. *Anal.* Calcd. for $C_{12}H_{13}O_4S_2Cl$: C, 44.93; H, 4.08; S, 20.00; Cl, 11.05. Found: C, 44.51; H, 4.06; S, 19.43; Cl, 10.89. UV $\lambda_{max}^{50\% H_2SO_4}$ 240, 271 (sh), 340 mμ (log ε 4.21, 3.96, 3.71). NMR: *n*-C_3H_7 8.78^{t}, 7.84^{m}, 6.31^{t} (J=7 cps), C-5H 1.30 τ (CF_3COOD).

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